Electrophosphorescence

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A Simple Carbazole/Oxadiazole Hybrid Molecule: An Excellent Bipolar Host for Green and Red Phosphorescent OLEDs**

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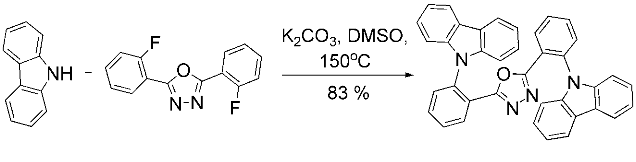
Phosphorescent organic light-emitting diodes (PHOLEDs) continue to attract intense interest because they can, in theory, approach a 100 % internal quantum efficiency by utilizing both singlet and triplet excitons.[1] To achieve highly efficient electrophosphorescence by reducing competitive factors such as concentration quenching and triplet–triplet annihilation, phosphorescent emitters of heavy-metal complexes are usually doped into a suitable host material.[2] Thus the synthesis of host materials and dopants are equally important for the formation of efficient PHOLEDs. It is desirable that the host materials have a large enough bandgap for effective energy transfer to the guest, good carrier transport properties for a balanced recombination of carriers in the emitting layer, and energy-level matching with neighboring layers for effective charge injection.

Recently, bipolar hosts have aroused considerable interests in the area of organic light-emitting diodes (OLEDs) because they can provide more balance in electron and hole fluxes and simplify device structure.[3] However, a compromise is required between the bipolar transporting property and band gap of the material, because the electron-donating and electron-withdrawing moieties in bipolar molecules unavoidably lower the band gap of the material by intramolecular charge transfer, while the low triplet energy of the host can cause reverse energy transfer from the guest back to the host, which consequently decreases the efficiency of PHOLEDs. To address this issue, most recent molecular designs focus on the interruption of the π conjugation between electron-donating and electron-withdrawing moieties by the incorporation of steric groups[4] and/or *meta* linkages[2,5] between the two moieties. Efficient blue ($46\,\mathrm{lm\,W^{-1}}$, 24 %),[2] green ($27.3\,\mathrm{cd\,A^{-1}}$)[4b] and orange ($22\,\mathrm{cd\,A^{-1}}$, 7.8 %)[4a] electrophosphorescence from such small bipolar host molecules has been reported.

Carbazole derivatives can be used as host materials because of their high triplet energy and good hole-transporting ability.[6] For example, 4,4′-*N*,*N*′-dicarbazolbiphenyl (CBP) is a popular host for triplet emitters. PHOLEDs that use CBP as a host material for various dopants have been reported to have peak efficiencies as high as $28\,\mathrm{cd\,A^{-1}}$ for green (*fac*-tris(2-phenylpyridinato-$N,C^{2'}$)iridium, [Ir(ppy)$_3$]),[1a] $52\,\mathrm{cd\,A^{-1}}$ for green (tris[3,6-bis(phenyl)-pyridazinato-$N^1,C^{2'}$]iridium [Ir(BPPya)$_3$])[7] and $5.82\,\mathrm{cd\,A^{-1}}$ for deep red (a dendritic iridium complex).[8] Unfortunately, the CBP host is prone to crystallization, especially when the dopant concentration is too low.[8,9] Furthermore, red PHOLEDs containing a CBP host usually need high driving voltages because the poor energy match between CBP and adjacent hole- and electron-transporting layers can result in insufficient and/or unbalanced injection of holes and electrons.[10] It is a worthwhile target to develop host materials with good thermal stability and matching energy levels to replace CBP. Oxadiazole derivatives have been proven to be very effective in improving the injection and transport of electrons. For example, 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD)[11] and 1,3-bis[4-*tert*-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD7)[11b] are usually incorporated in OLEDs as electron-transport materials.

Herein we report a novel carbazole/oxadiazole hybrid molecule *o*-CzOXD linked through the 9-position of carbazole with the *ortho* position of 2,5-diphenyl-1,3,4-oxadiazole. The bipolar molecule *o*-CzOXD was easily prepared by an aromatic nucleophilic substitution reaction between carbazole and the fluoroarene,[12] which was activated by the electron-withdrawing oxadiazole, with good yields of over 80 % (Scheme 1). The reaction proceeded in the absence of any catalyst, and the product was easily purified by recrystallization from $CHCl_3/C_2H_5OH$ rather than column chromatography. Thus, this simple method has obvious advantages over common palladium-catalyzed coupling reactions. *o*-CzOXD was characterized by ^1H NMR and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis; its molecular structure was further confirmed by X-ray crystallography (Figure 1).[13] The dihedral angle between the carbazole unit and the phenyl ring is 51.4°; this twist in the



Scheme 1. Synthesis of *o*-CzOXD.

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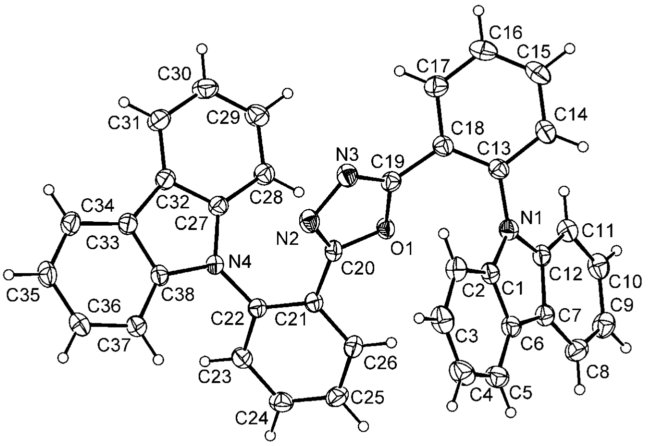

Figure 1. ORTEP diagram of *o*-CzOXD (thermal ellipsoids at 30°% probability).

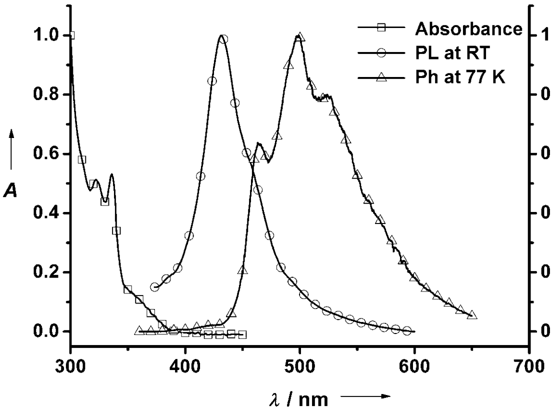

Figure 2. Absorption and emission (PL) spectra of *o*-CzOXD in $CHCl_3$ at room temperature, and phosphorescence (Ph) spectra of *o*-CzOXD in toluene at 77 K.

structure results in the reduction of the π conjugation between carbazole and oxadiazole moieties. The molecule has a high triplet energy level of 2.68 eV (calculated from phosphorescence spectra) and is a potential host for green, red, and even light blue phosphorescent dopants. Devices containing *o*-CzOXD as host show maximum external quantum efficiencies as high as 20.2% for green and 18.5% for deep red electrophosphorescence.

The thermal stability of *o*-CzOXD is shown by the high decomposition temperatures (T_d, corresponding to 5% weight loss) of 428°C in the thermogravimetric analysis. The glass transition temperature (T_g) of *o*-CzOXD was observed to be 97°C by differential scanning calorimetry (DSC), which is much higher than that of analogues CBP (62°C) and 1,3-bis(*N*-carbazolyl)benzene (*m*CP, 60°C).[14] The high T_g and T_d values of *o*-CzOXD may be attributed to the introduction of the rigid oxadiazole moiety, and can improve the film morphology and reduce the possibility of phase separation upon heating.[15]

The electrochemical properties of *o*-CzOXD were investigated by cyclic voltammetry (CV). The compound exhibits reversible oxidation and reduction behavior, which implies the formation of stable cation and anion radicals and confirms the potential of *o*-CzOXD for efficient electron/hole transport.[3,16] The HOMO–LUMO (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) energy levels determined from the onsets of the oxidation and reduction potentials are 5.55 and 2.56 eV (relative to vacuum level), respectively, which are significantly higher than the corresponding energies of CBP (HOMO: 6.0 eV, LUMO: 2.9 eV).[7]

Figure 2 shows the electronic absorption and fluorescence spectra of *o*-CzOXD. The absorption at 340 nm is attributed to π–π* transitions of carbazole.[6,14] The photoluminescence (PL) spectrum of *o*-CzOXD in $CHCl_3$ shows blue emission at 434 nm. The triplet energy of *o*-CzOXD was determined to be 2.68 eV from the highest energy vibronic sub-band of the phosphorescence spectrum at 77 K. This value is higher than that of CBP (2.56 eV), which indicates that *o*-CzOXD may be an appropriate host material for green, red, and even light blue phosphorescent emitters.

To evaluate the performance of *o*-CzOXD as host material, devices with the structures of indium titanium oxide(ITO)/MoO_3 (10 nm)/1,4-bis[(1-naphthylphenyl)amino]biphenyl (NPB, 40 nm)/Host: $[Ir(ppy)_3]$ (30 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 10 nm)/tris(8-hydroxyquinoline)aluminum ($[Alq_3]$, 30 nm)/LiF (1 nm)/Al (100 nm) were fabricated. NPB and $[Alq_3]$ were used as the hole- and electron-transporting materials, respectively, $[Ir(ppy)_3]$ doped into either *o*-CzOXD (devices A and C) or CBP (device B) as the emitting layer, BCP was used as hole and exciton blocking layer, and MoO_3 and LiF served as hole- and electron-injecting layer, respectively. The luminance-voltage-current density (L-V-J) characteristics of the devices examined in this work are shown in Figure 3 (efficiency versus current density curves are shown in Figure S1 in the Supporting Information). The device data are summarized in Table 1. Optimization studies showed that the best electroluminescence (EL) performance was achieved with 9 wt% addition of dopant. Device A (*o*-CzOXD as host) shows low turn-on voltages of 3.1 V and a maximum current efficiency (η_c) of 75.0 cd A^{-1} at a brightness of 220 cd m^{-2}; while device B (CBP as host), shows a turn-on voltage of

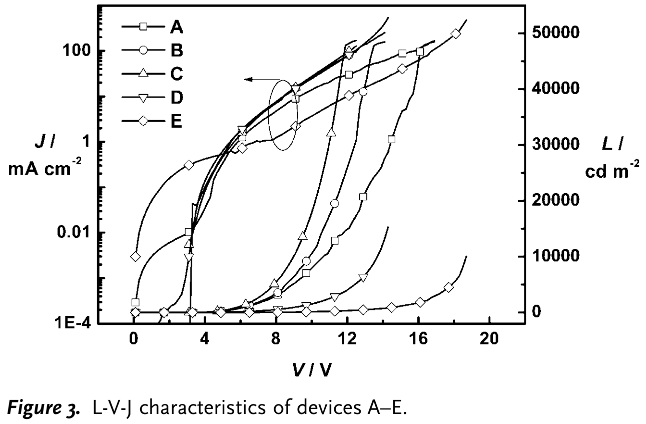

Figure 3. L-V-J characteristics of devices A–E.

Table 1: EL data for devices A–E.

Device (HTL/EML)[a] [nm]	Host/ guest[b]	$V^{[c]}$ [V]	L_{max} [cd/m^2],[d] voltages [V]	$\eta_{c.max}$[e] [cd A^{-1}]	$\eta_{p.max}$[f] [lm W^{-1}]
A(40/30)	*o*-CzOXD/Ir-G	3.1	48503, 16.9	75.0	51.4
B(40/30)	CBP/Ir-G	3.3	48464, 14.1	57.2	38.5
C(80/20)	*o*-CzOXD/Ir-G	3.1	48719, 12.5	77.9	59.3
D(80/20)	*o*-CzOXD/Ir-R	3.3	15289, 14.3	13.6	11.5
E(80/20)	CBP/Ir-R	5.3	10063, 18.7	3.4	1.2

[a] HTL/ETL = thickness of the hole transport and emitting layer, respectively. [b] Ir-G = [Ir(ppy)$_3$], Ir-R = [(piq)$_2$Ir(acac)]. [c] Turn-on voltage. [d] Maximum luminance. [e] Maximum current efficiency. [f] Maximum power efficiency.

3.3 V and a maximum current efficiency of 57.2 cd A^{-1} at a brightness of 251 cd m^{-2}. Device A exhibits much better EL performance than device B for three reasons. Firstly, as shown in the energy level diagram of Figure 4, the hole injection barrier of 0.6 eV from NPB to the CBP host is much higher than that of 0.15 eV from NPB to the *o*-CzOXD host. Secondly, [Ir(ppy)$_3$] (HOMO: 5.4 eV, LUMO: 2.9 eV)[7] has a hole trap with a depth of 0.6 eV in the CBP host, thus hole trapping may occur. But it has almost the same LUMO level as the CBP host, consequently, electron trapping is unfavorable. In contrast, the *o*-CzOXD host has a HOMO level 0.15 eV below and a LUMO level 0.45 eV above the dopant [Ir(ppy)$_3$], therefore both hole and electron can be trapped on the dopant sites directly, and exciton formation is more efficient than the CBP host. Thirdly, the *o*-CzOXD host has a higher triplet energy level (2.68 eV) than CBP (2.56 eV), thus it can efficiently suppress reverse energy transfer from guest to host. To further optimize the EL performance of green phosphorescent OLEDs, device C with the structures of ITO/MoO$_3$ (10 nm)/NPB (80 nm)/*o*-CzOXD : [Ir(ppy)$_3$] (20 nm)/BCP (10 nm)/Alq$_3$ (30 nm)/LiF (1 nm)/Al (100 nm) was fabricated. Since the hole mobility in NPB is about two orders of magnitude higher than electron mobility in [Alq$_3$],[17–19] the thickness of the NPB hole transport layer (HTL) was increased to 80 nm for device C (40 nm for device A) to add a time delay to hole transport and obtain a balance of hole and electron transport in EL devices. The optimized device C has a maximum current efficiency (η_c) as high as 77.9 cd A^{-1} at a brightness of 313 cd m^{-2}, equivalent to an external quantum efficiency (η_{EQE}) of 20.2 %. When the brightness reached 10000 cd m^{-2}, η_c is still as high as 68.8 cd A^{-1} ($\eta_{EQE} = 17.9$ %). These values are much higher than those of similar devices containing CBP[1a] or 3-(4-biphenyl)-4-phenyl-5-*tert*-butylphenyl-1,2,4-triazole (TAZ),[20] and even comparable with those with double emissive layer p-i-n structured devices (in which an intrinsic emission layer is embedded between n- and p-type doped large-gap transport layers).[21] To the best of our knowledge, the performance of this device is among the highest for green phosphorescent OLEDs reported to date.

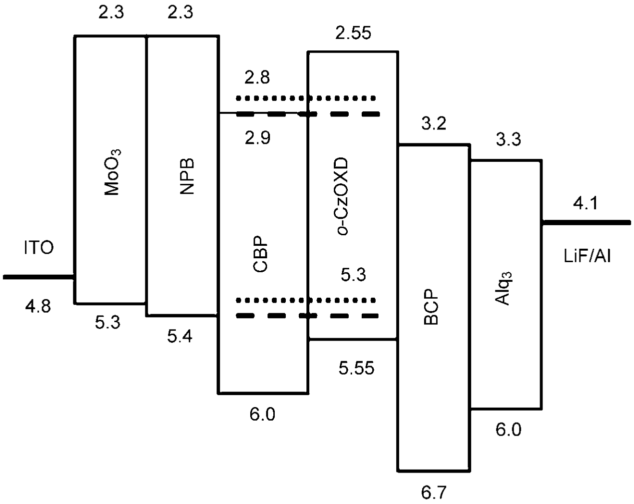

Figure 4. Energy level diagram of HOMO and LUMO levels for materials investigated in this work. Energy levels of [Ir(ppy)$_3$] (dashed line) and [(piq)$_2$Ir(acac)] (dotted line) are also shown.

To further verify the superior host properties of *o*-CzOXD, red phosphorescent OLEDs with composition ITO/MoO$_3$ (10 nm)/NPB (80 nm)/host: bis(1-phenylisoquinolinolato-C^2,N)iridium(acetylacetonate) ([(piq)$_2$Ir(acac)], 6 wt %, 20 nm)/BCP (10 nm)/[Alq$_3$] (30 nm)/LiF (1 nm)/Al (100 nm) were fabricated. Device D (*o*-CzOXD as host) emits deep red light with CIE (Commission Internationale de l'Eclairage) values of 0.68 and 0.32, and shows the best EL performance, with a maximum luminance of 15289 cd m^{-2} at 14.3 V, a maximum current efficiency of 13.6 cd A^{-1} (equivalent to η_{EQE} of 18.5 %), and a power efficiency of 11.5 lm W^{-1}. To the best of our knowledge, the efficiencies of device D are the highest among reported red phosphorescent OLEDs with similar CIE values. We note that device D exhibits much better EL performance and significantly lower turn-on voltages than the CBP-containing device E (3.3 V to 5.3 V). Furthermore, the discrepancy in EL performance between devices D and E was significantly larger than that between devices A and B. This may be attributed to the more suitable energy-level matching for the host and the guest in device D. The red dopant [(piq)$_2$Ir(acac)] has HOMO and LUMO levels of 5.3 and 2.8 eV, respectively.[22] Thus it has a deep hole trap of 0.7 eV in the CBP host; its LUMO lies 0.1 eV higher than CBP, so direct exciton formation on the dopant site is less efficient. In contrast, the HOMO and LUMO levels of [(piq)$_2$Ir(acac)] fall within those of the *o*-CzOXD host, with a shallow hole and electron trap depth of 0.25 and 0.35 eV, respectively, which leads to a more balanced charge trapping and recombination, and more efficient energy transfer from the *o*-CzOXD host to the guest compared to CPB-containing device E.

In summary, we have developed a convenient and efficient synthesis of a novel carbazole/oxadiazole hybrid molecule. This methodology can be used to easily combine various arylamines and electron-deficient arenes with fluorine substituents to prepare bipolar molecules. The twisted structure formed by linking the 9-position of carbazole with the *ortho* position of 2,5-diphenyl-1,3,4-oxadiazole results in good thermal and morphological stabilities and a high triplet energy level. Devices containing the *o*-CzOXD host show maximum external quantum efficiencies as high as 20.2 % for green and 18.5 % for deep red electrophosphorescence, which are much higher than those of identical devices with the CBP host. These outstanding EL performances are attributed to the well-matched energy levels between the host and hole transport layer, as well as between the host and the dopant, which consequently leads to a more balanced injection and recombination of charge carriers. The merits of the simple bipolar host *o*-CzOXD make it an ideal substitute for the most widely used host CBP. The evaluation of the lifetime of devices that incorporate the *o*-CzOXD host is in progress.

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